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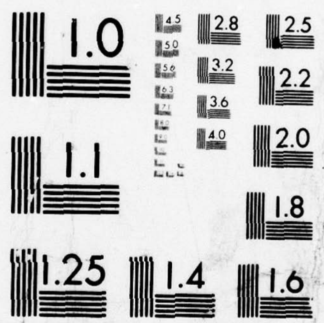

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DEVELOPMENT OF HIGH RADIATION OUTPUT

INFRARED CHEMILUMINESCENT SYSTEMS

FINAL REPORT

TO THE

U. S. ARMY RESEARCH OFFICE

DURHAM, NORTH CAROLINA

CONTRACT DAAG29-76-C-0047

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Bound Brook, New Jersey

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An infrared-emitting chemiluminescent system with no visible emission has been discovered. Spectral maximum is at 790 nm. Lifetime is about 30 minutes, but catalysis can be varied to lengthen lifetime. This new system is based on the reaction of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate with hydrogen peroxide in the presence of the infrared fluorescer, 16,17-didecyloxyviolanthrone.

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SUMMARY

An infrared-emitting chemiluminescent formulation with no significant visible emission has been discovered. This system has a spectral maximum of 790 nm (see Figure A) and a maximum radiation capacity of about 790 joules liter^{-1}. The lifetime of the new system is about 30 minutes (see Figure B) but catalysis can be varied to produce shorter or longer lifetimes with minimal losses in radiation capacity. This new system is based on the reaction of bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) with hydrogen peroxide in the presence of the infrared fluorescer 16,17-didecyloxyviolanthrone (DDV). The greater solubility of DDV compared to the previous best IR fluorescer, 16,17-dihexyoxyviolanthrone, allows concentrations up to .006M to be attained thus increasing the amount of self-absorption, effectively eliminating any visible emission. Purity of DDV was critical in eliminating visible emitting impurities. Extensive purification procedures including repeated recrystallizations and preparative high performance liquid chromatography was required to remove traces of visible emitting impurities.

The new system has been formulated into the solvent mixture currently used for a number of visible chemical light products: 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol. This provides a high flash point, low toxicity, low odor vehicle for the IR chemiluminescent reaction. Storage stability of the new system has not been evaluated, but experience with similar formulations indicates this probably will be satisfactory.

FIGURE A: SPECTRAL DISTRIBUTION OF IR CHEMILUMINESCENT SYSTEM

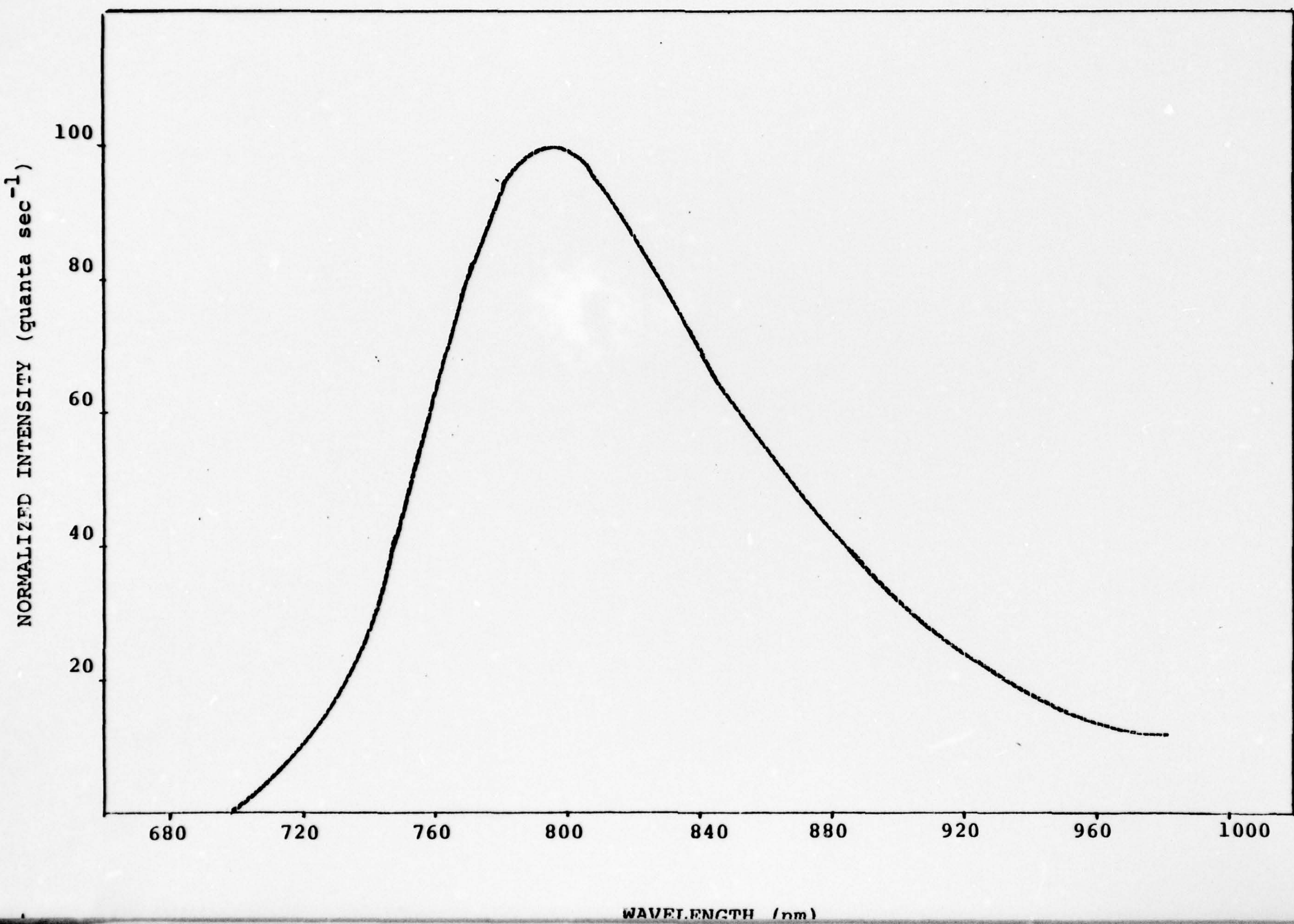
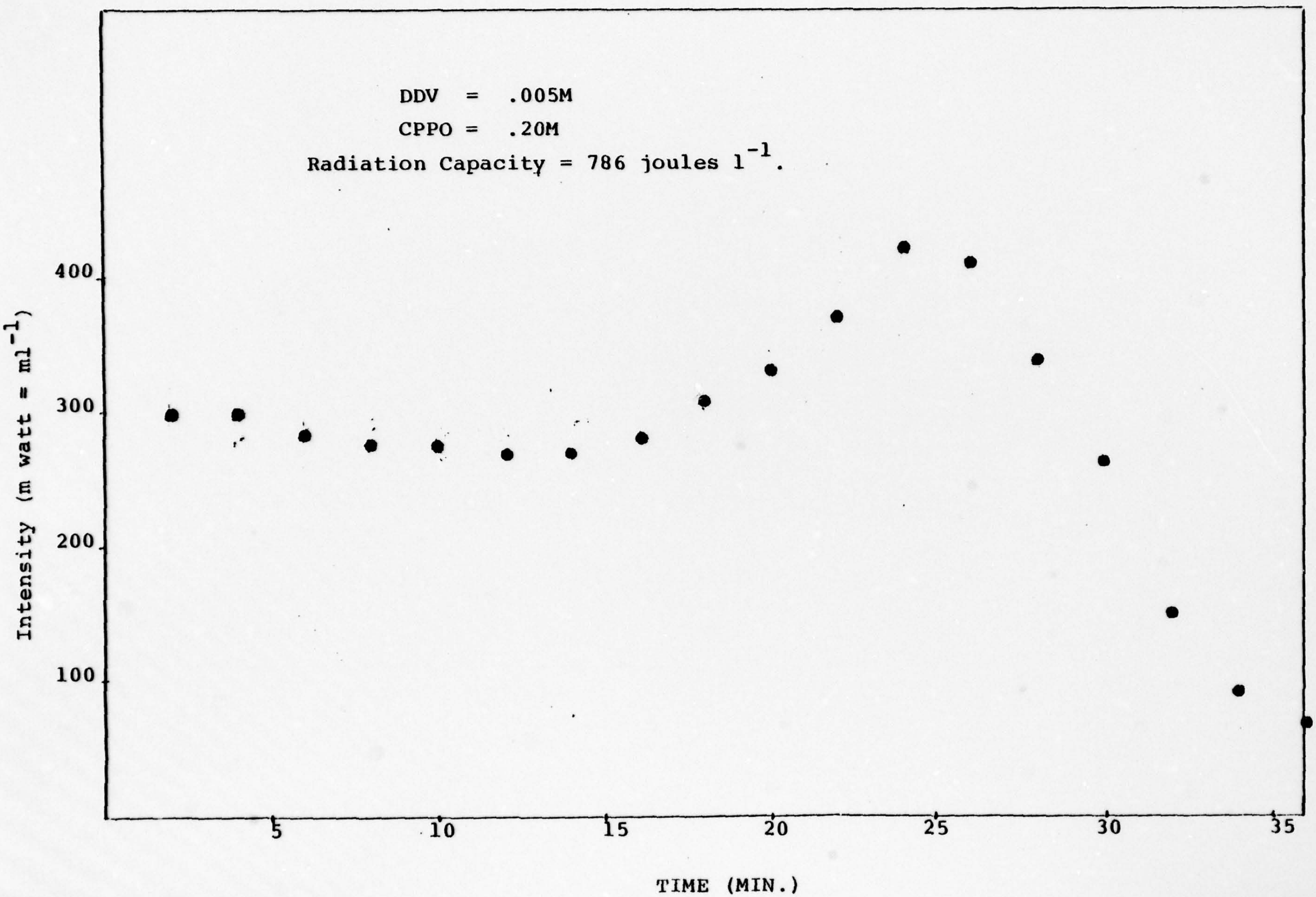


FIGURE B: INTENSITY-TIME DISTRIBUTION OF IR CHEMILUMINESCENT REACTION



Introduction

Background

The American Cyanamid Company has conducted research on chemiluminescence since 1961[1,2] with the objective of exploiting the inherent capabilities of chemiluminescence through the development of practical marking and illumination systems. The attractive potential of chemiluminescence is based on:

(1) A high theoretical light energy density of 173,000 lm. hr l^{-1} equivalent to the light output of a 40 watt incandescent bulb burning continously for 2 weeks. This high energy density makes chemiluminescence especially suited for portable lighting applications and for other applications where the use of distributed power is inconvenient or impossible. The equivalent theoretically optimum infrared radiant energy density is 770,000 joules liter^{-1}.

(2) Chemiluminescence is cold light. Since heat and flame are absent, chemiluminescent systems can be used where a conventional hot light would cause fire or explosion. Automobile and aircraft accident sites, coal mines and repair of gas transmission lines are examples.

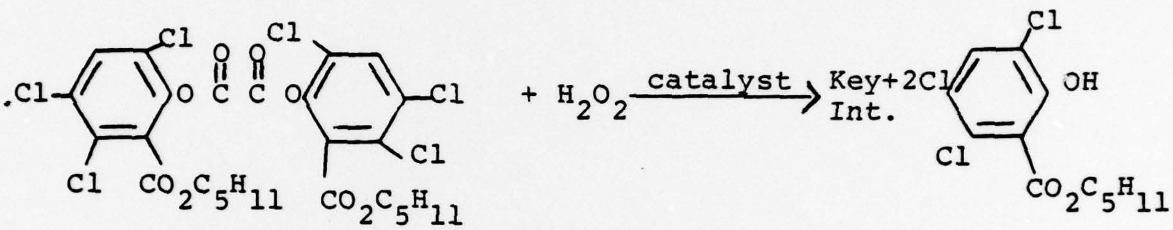
(3) Reliability through long shelf life. Conventional battery systems gradually lose energy even when in storage. Chemiluminescent systems, in principle, can have indefinite storage lifetimes.

Chemiluminescent reactions with the efficiency required for practical use were unknown at the beginning of Cyanamid's program. Even the fundamental chemistry required for the discovery of new chemiluminescent reactions was unavailable.

Following initial feasibility studies[3], a detailed mechanism study was begun in 1963 under Contract NONR 4200(00) with the Office of Naval Research to obtain the basic knowledge required to design efficient chemiluminescent reactions. This effort was successful[4] and led to the discovery of practical chemical light formulations under subsequent contracts with the U.S. Naval Ordinance Laboratory[5,6] (contract numbers N60921-67-C-0214 and N60921-70-C-0198). As a consequence of these programs, the light output efficiency of chemical light was increased more than 1600 times[7]. Under a later contract with the U.S. Naval Weapons Center (contract number N00123-71-C-1069) the light output efficiency was increased an additional 3-fold[8]. Concurrent with the later contracts, Cyanamid conducted an independent applied research and development program[9] which developed one of the efficient formulations, peroxyoxalate chemiluminescence, into a practical chemical light system which is currently being used in commercial and governmental applications.

Peroxyoxalate Chemiluminescence

The first non-biological chemiluminescent reaction capable of high quantum efficiencies[2,3,4] was based on the reaction of certain oxalic esters with hydrogen peroxide in the presence of a fluorescent compound as illustrated by the reaction of bis (2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO) shown below:

1. 

2. Key Int. + Flr $\longrightarrow$ Flr* + $2CO_2$

3. Flr* $\longrightarrow$ Flr + Light

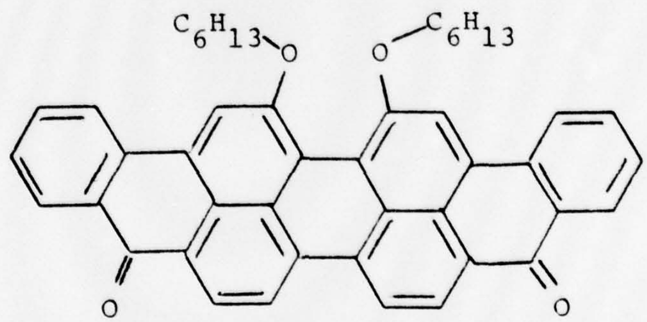
The reaction proceeds in three distinct steps. Step 1 leads to the formation of a key intermediate, believed to be 1,2-dioxetanedione, C_2O_4, which is catalytically decomposed in the presence of a fluorescent compound, Flr, converting the fluorescent compound to its first excited singlet state, Flr*. Radiative de-excitation of the excited molecule in step 3 is the source of light emission. A major advantage of this chemiluminescent system is that the structure of the fluorescent compound can be varied to provide a variety of colors spanning the visible region of the spectrum or to provide chemiluminescence emission in the infrared region.

In 1967, Cyanamid undertook the invention of liquid phase infrared chemiluminescence under contract DA8821-67-C-0503 administered by the Pyrotechnics Laboratory of the Picatinny Arsenal. Although liquid phase infrared chemiluminescence was unknown at the start of that effort, it was believed that the versatility of oxalic ester chemiluminescence would provide a feasible basis for its invention. This belief proved justified[10] and an infrared formulation developed under the Picatinny Arsenal contract has been patented[11]. This study has been described in detail in the final report of the contract[10] and a part of the work has been published[12]. The original formulation was later improved as a part of a larger program under contract N60921-70-C-0198 with the Naval Ordinance Laboratory[6].

Infrared chemiluminescent formulations then available, however, generated an unacceptable amount (1.6%) of visible light. Moreover, the extension of chemiluminescence knowledge since the earlier work has been substantial, and far more efficient infrared chemiluminescent formulations can now be developed. A new formulation providing high infrared intensity in the absence of visible light would substantially expand the utility of infrared chemiluminescence.

Infrared Chemiluminescence

An extensive screening program to discover efficient infrared fluorescers was carried out as part of the initial infrared chemiluminescence research program carried out under contract (DAAA21-67-C-0503) with Picatinny Arsenal[10]. The first organic infrared fluorescer, DHV, was synthesized as part of that program. Formulation of DHV with an early oxalate ester



16,17-Dihexyloxyviolanthrone (DHV)

provided the first example of liquid phase infrared chemiluminescence[10,11,12].

The discovery of the much more efficient oxalate ester, CPPO, in a subsequent contract[5] with the Naval Ordnance Laboratory permitted formulation of a substantially more efficient DHV-based system in 1971[6]. This system although providing a radiation capacity of 550 joules per liter, is not completely covert since 1.6% of its radiation is below 700 nm in the visible region of the spectrum. This fraction of visible radiation, although small, makes the system readily detectable by the unaided eye and therefore not completely covert.

Objectives

The primary objectives of this research program were (1) to develop a high intensity infrared emitting chemiluminescence system which is virtually invisible to the unaided eye and (2) to provide such catalysis or highly reactive oxalic acid derivatives to shorten the lifetime of the infrared system to less than two minutes. Major emphasis was placed on fluorescer design and synthesis since this was deemed essential for all applications of infrared chemiluminescence regardless of the lifetime requirement.

Infrared Fluorescer Design and Synthesis

A satisfactory infrared fluorescer must meet the requirements listed in Chart I.

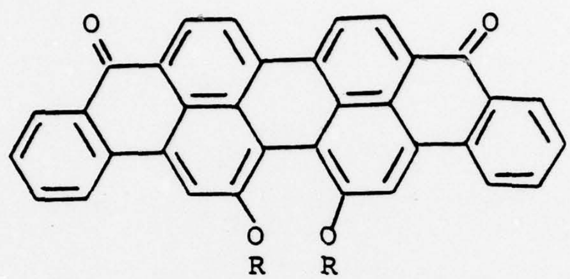
Chart I

Infrared Fluorescer Requirements

1. Zero emission below 700 nm and a spectral maximum near 800 nm.
2. Fluorescence quantum yield greater than 35%.
3. Ability to accept chemical excitation energy.
4. Solubility greater than 3×10^{-3} molar in phthalate ester solvents.
5. Stability to the reacting system.
6. Storage stability.
7. Moderate cost.
8. Low toxicity.

Previous experience has well documented the difficulty of designing fluorescers which meet all of these requirements and has indicated that requirements 5 and 6 in particular, while seemingly innocuous, are accommodated by very few structural classes.

Prior to the present work, the most efficient current infrared chemiluminescent system comprised the oxalate ester CPPO and the fluorescer 16,17-dihexyloxyviolanthrone (DHV)[6].



DHV: R= n-C_6H_{13}

DBV: R= $\overset{O}{\overset{\|}{C}}$-$C_6H_5$

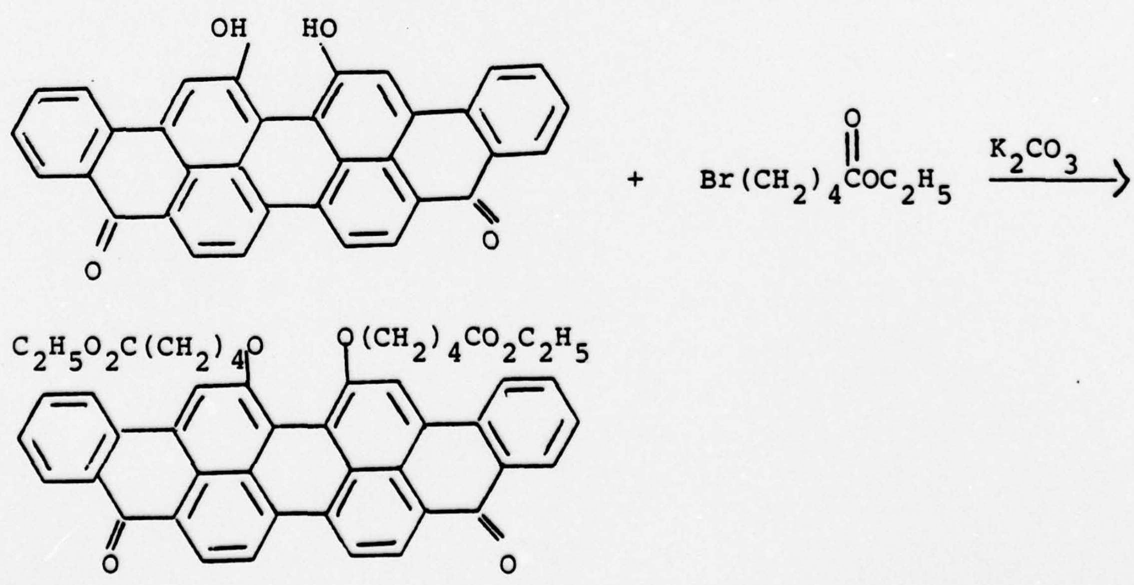
DPEV: R=$CH_2CH_2C_6H_5$

DCEV: R=$\overset{O}{\overset{\|}{C}}$-$OC_2H_5$

DHV has a solubility limit near 1.5 x 10^{-3}M in dibutyl phthalate, the preferred solvent for the chemiluminescent formulation. As described below, this concentration is too low for complete elimination of the visible light. One approach to eliminate the small fraction of visible light is to modify the basic DHV structure to increase the solubility in dibutyl phthalate. This will increase the amount of overlap between the absorption and emission bands causing self-absorption of the shorter (visible) wavelength emission and re-emission at longer wavelengths. This "internal-filtering" should then eliminate the visible radiation with only small losses in efficiency.

Earlier efforts to modify the structure of DHV by introducing ester groups as in DBV and DCEV were unsuccessful because of large shifts to shorter wavelengths giving predominantly red-emitting reactions. This shift is probably caused by the presence of the electron attracting carbonyl substituents on the violanthrone chromophore. However, synthesis of DPEV enabled the solubility to be improved two-fold over DHV (from 1.5×10^{-3}M to 3.0×10^{-3}M), thus causing a bathochromic shift of the spectral maximum from 770 nm to 820 nm with a concurrent decrease in visible emission from 3.3% to 2.1%. This result demonstrates that the self-absorption/re-emission principle is a valid approach to the elimination of the visible emission.

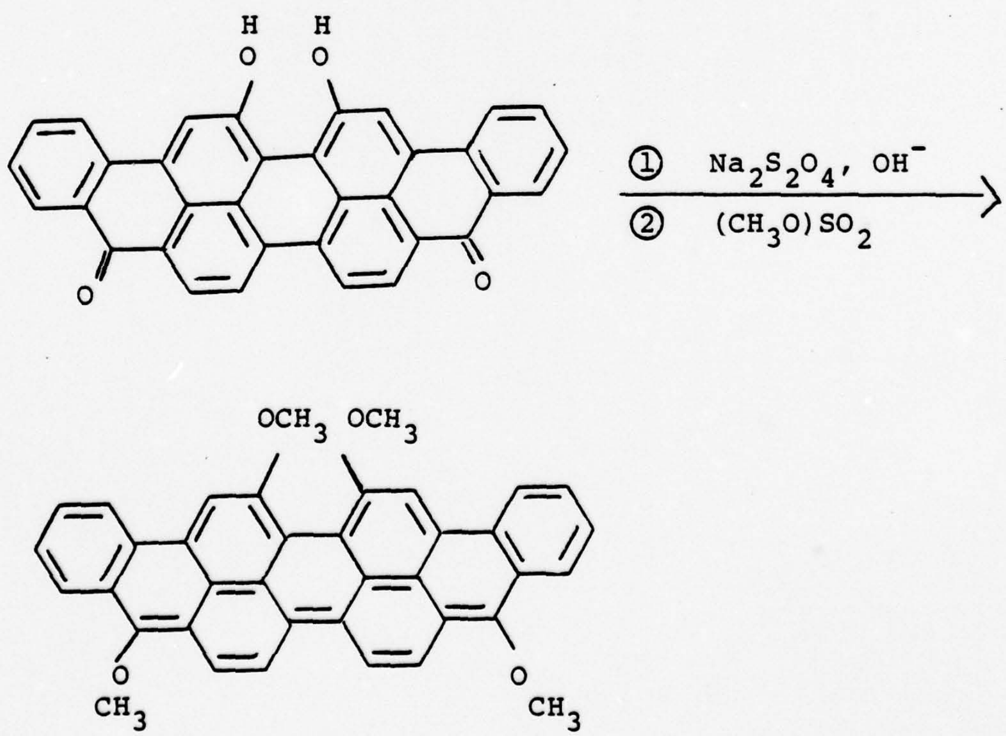
Research was therefore directed towards further improvements in the solubility of DHV. Compound CBV was prepared by the scheme outlined below as one of the early attempts to improve the solubility of DHV, the idea being that the ester "tail" of CBV should be more compatible with the phthalate ester solvents.



CBV

A chemiluminescent reaction with CPPO at .15M and CBV as the fluorescer gave quantum yield of 4.9% with a spectral maximum of 810 nm. However, 2.5% of the emission was in the visible region of the spectrum. The solubility of CBV was improved to 3.5×10^{-3}M in dibutyl phthalate, but this apparently is not sufficient to produce the "internal filter" effect via self-absorption.

Another approach to eliminate the small fraction of visible emission is to extend the conjugation of the aromatic system. Venkataramon[13] and co-workers have described a method for converting 16,17-dihydroxyviolanthrone to 5,10,16,17-tetramethoxyviolanthrone (1) via the "leuco" form:



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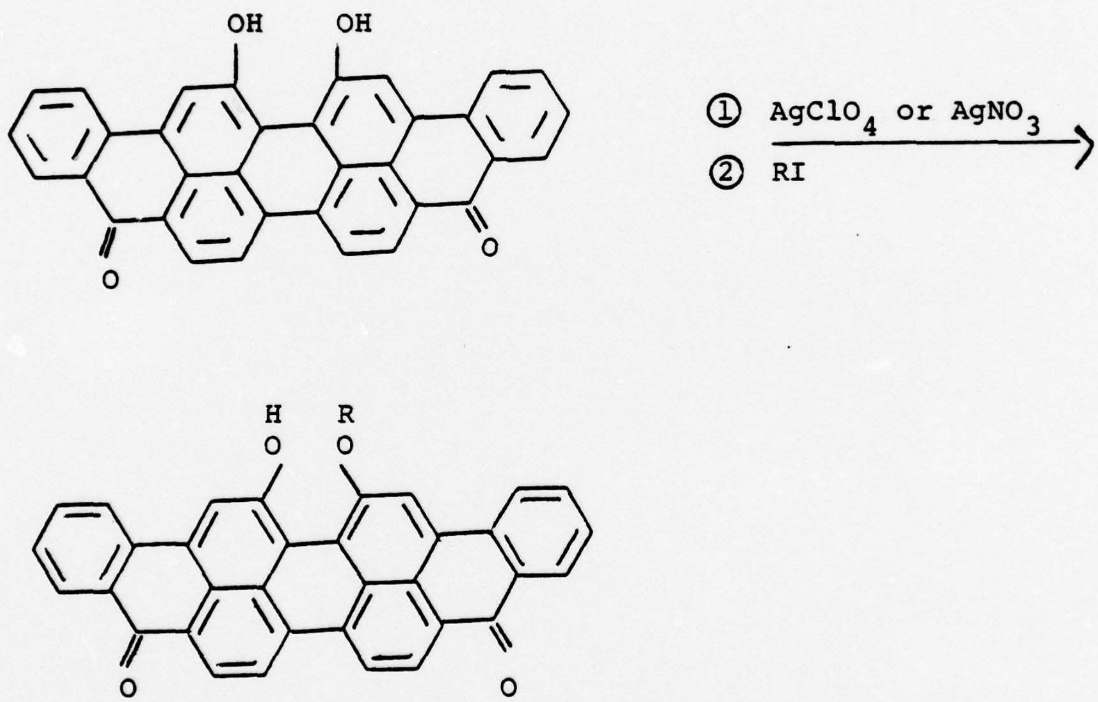
Compound 1 gave a red emission and was rapidly decomposed under the conditions of the chemiluminescent reaction and therefore was of no use as an infrared fluorescer.

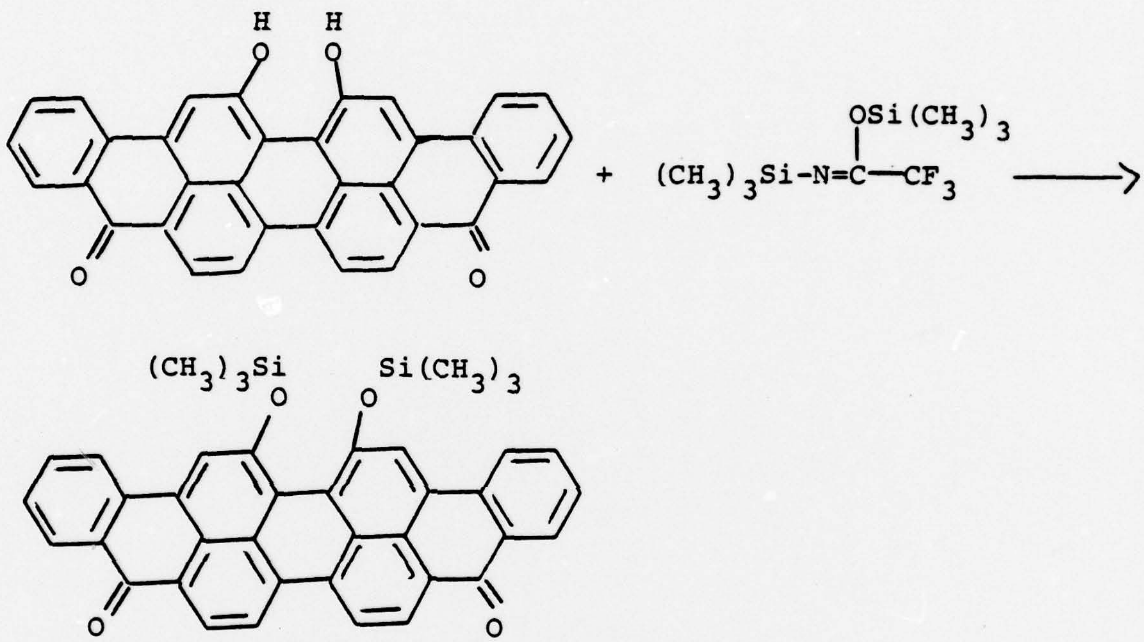
A new technique to prepare monoethers of dihydroxyviolanthrone was developed. This method uses the silver salt as an intermediate, which is then alkylated with the appropriate alkyl iodide to yield the respective mono ethers.



2 a. R = $(CH_2)_9CH_3$; mp 210°

b. R = $(CH_2)_{11}CH_3$; mp 204°

Monoethers 2a and 2b were prepared in the above manner. Chemiluminescent spectra from reactions containing 2a and 2b revealed 29% and 23% emission in the visible region. 16,17-Bis(trimethylsilyloxy)violanthrone (4) was prepared via the route indicated:



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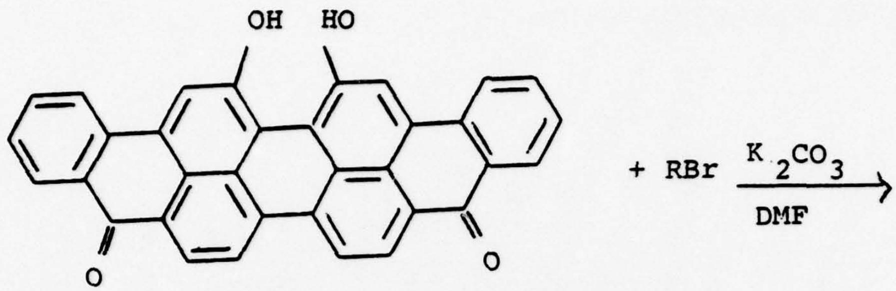
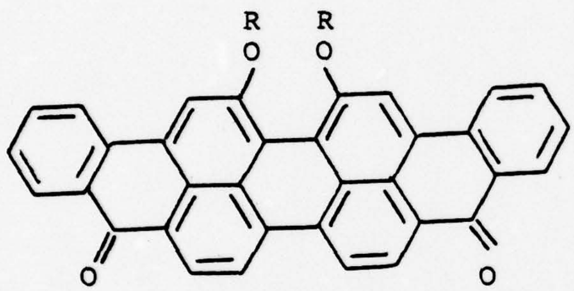
Compound 4 had 39% of its emission below 700 nm in the visible spectral region.

As described above, the dihexyl ether of violanthrone (DHV) was the first fluorescer found to have most of its emission in the infrared region, but a solubility limit of 1.5×10^{-3}M in dibutyl phthalate prevented significant self-absorption to eliminate the 1.9% visible emission. Two higher homologs 5 and 6 were prepared in an attempt to increase the solubility in the phthalate solvent. The method used was basically the same as

used for the preparation of the dihexyl derivative:





<u>5</u> R = $(CH_2)_9CH_3$ (DDV)

<u>6</u> R = $(CH_2)_{11}CH_3$

Compound DDV had a solubility limit of 8 x 10^{-3}M more than five times that of the dihexyl analog. After extensive purification including preparative high performance liquid chromatography, chemiluminescent reactions containing DDV revealed no detectable visible emission. The presence of trace amounts of visible-emitting impurities in the DDV necessitated the extensive purification procedures. The chemiluminescent performance of DDV is discussed in the evaluation section beginning on page 22.

SYNTHESIS OF NEW CHEMILUMINESCENT MATERIALS

Concepts

One of the objectives of this research is a very short lifetime (less than 2 min.) infrared chemiluminescent reaction with high radiation capacity. Previous research[4,5] on visible emitting systems has established that weakly basic salts such as sodium or potassium salicylate can be effective catalysts in the peroxyoxalate chemiluminescent reaction. As the catalyst concentration is increased the lifetime is decreased. However, when the catalyst level is increased sufficiently, a substantial loss in efficiency is observed. Table 1 illustrates such an example. As the catalyst concentration is increased from 0.5×10^{-3} to 3.0×10^{-3}M, the chemiluminescent quantum yield decreases from 2.9% down to 1.7% with a proportional reduction in radiation capacity. These results indicate that further increases in catalyst concentration to attain still shorter lifetimes would cause further decreases in radiation capacity. The efficiency loss is probably due to decomposition of a key chemiluminescent intermediate promoted by the high catalyst level.

TABLE ONE

EFFECT OF CATALYST CONCENTRATION ON CHEMILUMINESCENT PERFORMANCE OF DDV[1]

Catalyst[2] Conc. $M \times 10^3$	Quantum[3] Yield $\times 10^2$	T.75[4]	Radiation Capacity[5]
0.5	2.90	18.5	630
1.3	2.28	8.7	496
3.0	1.71	3.4	383

[1]Chemiluminescent reaction contained 6×10^{-3}M 16,17-didecyloxy-violanthrone (DDV), 0.15M bis(2,4,5-trichloro-6-carbopentoxy-phenyl)oxalate (CPPO) and .375M hydrogen peroxide in a solvent mixture of 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butanol (by volume).

[2]Catalyst was potassium salicylate.

[3]Chemiluminescent quantum yield in Einsteins $mole^{-1}$ of CPPO.

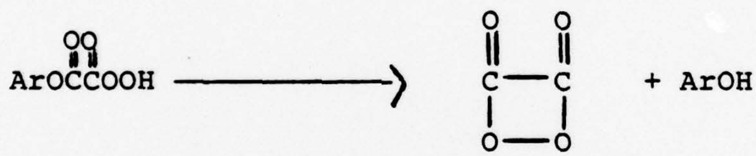
[4]Time (min.) required for 75% of the total radiation to be emitted.

[5]Total radiation output in joules l^{-1}.

High catalyst concentrations should be avoided to attain the requirement of short lifetime while maintaining efficiency. One promising approach to this problem is to design a oxalic acid derivative which reacts much more rapidly than the ester currently used, bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO). The following sections describe synthetic efforts to prepare such reactive oxalic acid derivatives.

1. <u>Cyclic Oxalates Based on Catechol</u>

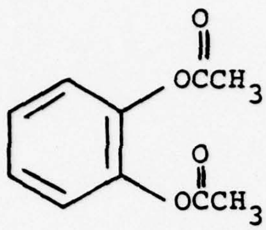
One of the key steps in the mechanism of peroxyoxalate chemiluminescence appears to involve cyclization of a monoperoxy oxalic acid intermediate to the dioxetanedione (eq. 1):

(1) 

The key to the high efficiency of the peroxyoxalate system may be due to the high yield in this step. A high proportion of the monoperoxy oxalic acid undergoes the desired cyclization process at the expense of other side reactions which would consume the monoperacid and lower the overall chemiluminescence efficiency. A good leaving group (ArOH) will promote this cyclization as well as the initial displacement by hydrogen peroxide.

Studies on the hydrolysis of catechol monoacetate (<u>1</u>) and diacetate (<u>2</u>) have shown the mono acetate hydrolyzes much faster than the diacetate, presumably due to the effect of hydrogen

bonding in the mono ester promoting the hydrolysis. This effect



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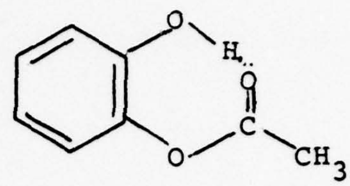

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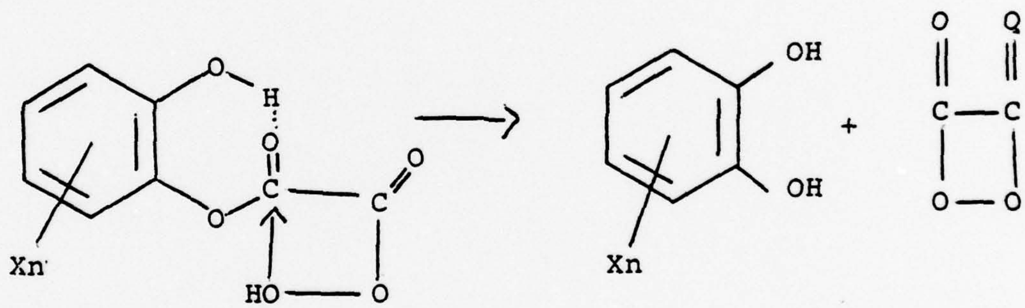
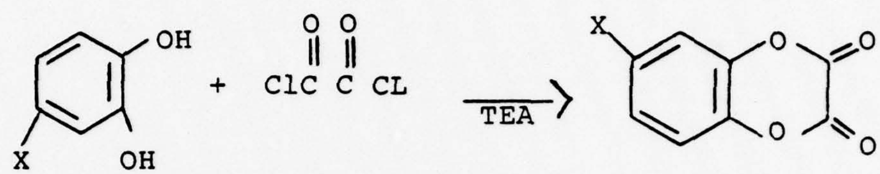
should be applicable to the peroxyolate system in that an appropriately substituted catechol should undergo the cyclization quite readily (eq. 3):

(3)



One or more electron attracting groups (X_n) will probably be required to maximize the reactivity. Two additional benefits will result from these cyclic oxalates (1) the molecular weight will be lower so solubility in g/l can be proportionately lower and (2) the concentration of the phenolic by-product, a possible quencher will be halved thus improving efficiency.

Treatment of the appropriately 4-substituted catechols with oxalyl chloride in the presence of triethylamine afforded the 6-chloro and 6-nitro oxalic esters. The nitro compound (4) proved to be quite sensitive to atmospheric moisture

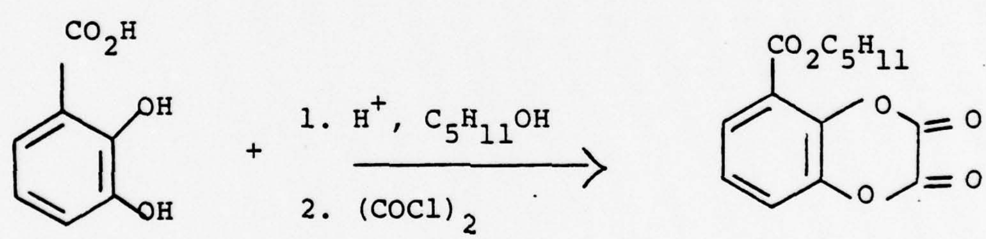


3 x = Cl

4 x = NO_2

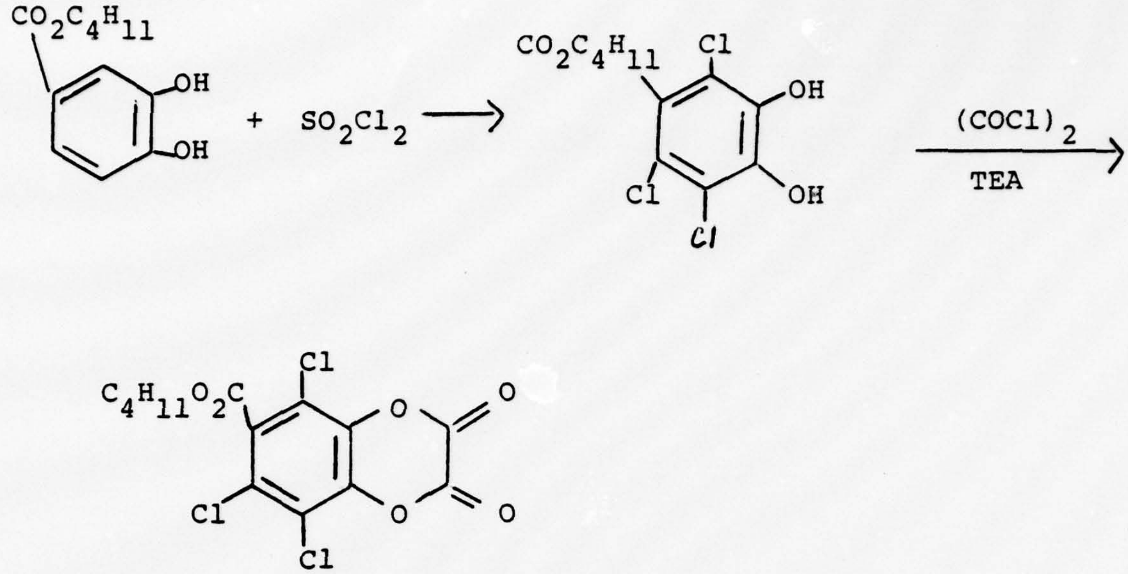
and had to be stored in a dessicator.

The pentyl ester was prepared by direct esterification of 2,3-dihydroxybenzoic acid with n-pentanol followed by oxalylation as above:



The isomeric 6-carbopentoxy derivative was prepared in a similar manner.

The butyl ester of 3,4-dihydroxybenzoic acid converted to the trichloro derivative by treatment with sulfuryl chloride and esterification with oxalyl chloride in the usual manner gave cyclic oxalate ester 5.



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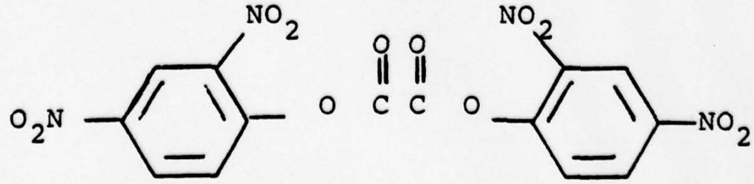
2. Other Oxalic Acid Derivatives

The oxalic ester[5] derived from 2,4-dinitrophenol is one of the most efficient oxalic esters known, with chemiluminescent quantum yield of 25% reported . Compound 6 suffers from poor solubility , but is quite reactive even without basic catalysis. In view of the very good performance of oxalates derived from chlorinated salicylic acid esters, a related ester, 6, was prepared by the route outlined on the next page.



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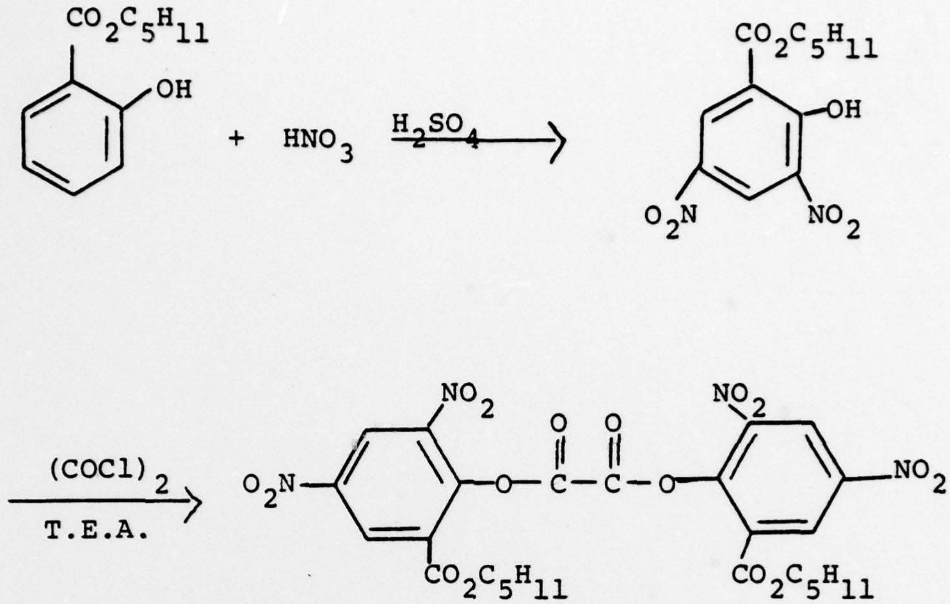

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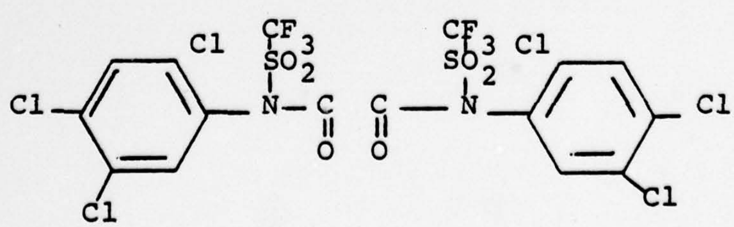
Very recent results[14] from these laboratories has revealed the discovery of new class of highly efficient chemiluminescent materials based on N-trifluoromethylsulfonyl substituted diaryl oxamides. Chemiluminescent quantum yields of 34% were reported for the oxamide 8. As in the case of the oxalic esters, increasing electronegative substitution on the aromatic ring shortens the lifetime and improves the efficiency. The polyfluorinated derivative 9 was therefore prepared the the route outlined below in an attempt to increase the reactivity while maintaining the high efficiency of the N-triflic oxamide series.



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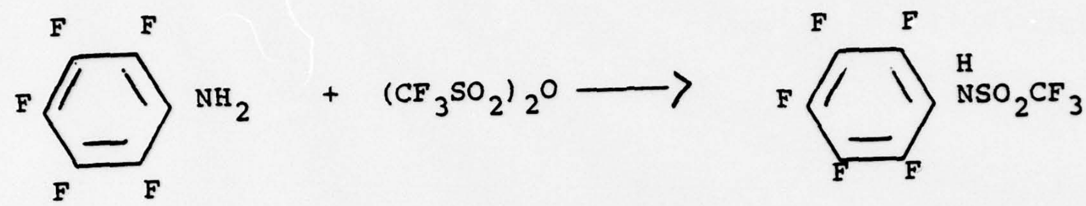

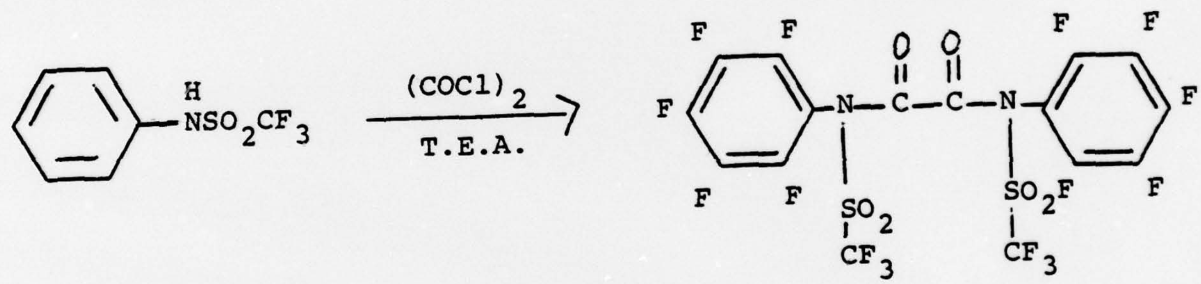

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EVALUATION OF NEW IR SYSTEM

1. Spectral Distribution

Increasing the concentration of the infrared fluorescer DDV in the chemiluminescent reaction should decrease the fraction of visible light because of self-absorption and re-emission. Results summarized in Table 2 show that this, in fact, does occur although the amount of visible light produced is very small and not observable within the concentrations studied. The composite spectra illustrated in Figure 1 shows that the lower wavelength slope of the spectrum steadily shifts to longer wavelength although a corresponding change in the wavelength of the spectral maximum is not observable.

2. Formulation Optimization

A set of experiments designed to determine the optimum concentrations of fluorescer and oxalate ester is summarized in Table 3. A relatively high (7.5×10^{-4}M) catalyst level was used in these experiments to obtain short-lifetime chemiluminescent reactions. The radiation capacity as would be expected, increases with increasing oxalate ester concentration, but it is interesting that the <u>highest</u> efficiencies (quantum yields) are obtained at the highest oxalate levels. This contrasts with the typical visible emitting reactions where the highest efficiency is usually found at the lowest oxalate concentrations because of concentration quenching. The optimum DDV level is at .004M, but

.005M is probably preferred since only slight reduction in radiation capacity occurs at this concentration and visible emission is also reduced. Moreover, storage stability of formulations generally improve with higher fluorescer concentrations.

3. New chemiluminescent Materials

Performance data on three new chemiluminescent materials is summarized in Table 4. Although short lifetimes were obtained for all three compounds tested, the efficiencies (quantum yields) and radiation capacities were much too low for consideration in practical IR formulations. Typical systems based on CPPO, the current oxalic ester of choice, give radiation capacities in the 750 to 790 joules liter^{-1} range.

TABLE 2

EFFECT OF FLUORESCER CONCENTRATION ON AMOUNT OF VISIBLE LIGHT FROM IR SYSTEM[1]

DDV Conc. M x 10^{-3}	% Visible x 10^{-3}	max[2]
6.00	4.3	790 nm
	4.0	790
5.00	4.9	790
	5.0	780
	4.8	780
4.00	6.5	790
	6.2	790
	4.1	790
3.00	6.4	790
	6.5	780
	6.6	780

[1]All reactions contained 0.15M bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO), 7.5 x 10^{-4}M sodium salicylate, .375 M H_2O_2, and the indicated concentrations of 16,17-didecyloxy violanthrone (DDV). Solvent concentrations: 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butyl alcohol.

[2]Emission maxima of chemiluminescence in quanta sec^{-1} and microwatts coincided.

TABLE 3

EFFECTS OF FLUORESCER AND OXALATE CONCENTRATION ON PERFORMANCE OF IR SYSTEM

DDV CONC (1)	CPPO CONC. M	RC (2)	Q.Y. (3) x 10^2	T.75 (4)	INTENSITY (in watt ml^{-1}) Vs. Time (Min.) 0	2	4	10	20	30
.003	.05	107	1.44	25	633	95	88	88	88	135
		96	1.30	25	573	95	88	81	101	121
	.10	299	2.00	12	1643	263	296	296	95	88
		294	1.99	12	1542	249	290	296	101	115
	.15	558	2.52	14	2013	371	377	438	74	41
		557	2.51	13	2485	357	364	450	54	34
	.20	718	2.43	25	1744	337	337	323	323	182
		740	2.50	26	1140	330	323	310	317	189
.004	.05	105	1.44	24	627	92	100	77	123	130
		113	1.55	25	650	107	100	100	107	130
	.10	302	2.07	11	1683	260	299	337	100	130
		298	2.04	11	1728	276	299	314	92	130
	.15	568	2.59	12	2440	360	375	505	54	46
		569	2.60	12	2360	344	367	513	54	46
	.20	831	2.85	26	1981	352	337	321	390	184
		749	2.56	24	2280	344	329	306	375	176

(1) Concentrations of 16,17-didecyloxyviolanthrone (DDV) and bis(2,4,5-trichloro-6-carbopentoxy-phenyl oxalate (CPPO) are in the chemiluminescent reaction containing .375 M H_2O_2 and 7.5 x 10^{-4}M sodium salicylate as catalyst. Solvent system was 75% dibutyl phthalate, 20% dimethylphthalate, 5% t-butyl alcohol.

(2) Radiation capacity in joules $liter^{-1}$.

(3) Chemiluminescent quantum yield in einsteins $mole^{-1}$.

(4) Time for 75% of the total radiation to be emitted.

TABLE 3 (Cont'd)

EFFECTS OF FLUORESCER AND OXALATE CONCENTRATION ON PERFORMANCE OF IR SYSTEM

DDV CONC (1)	CPPO CONC. M	RC (2)	Q.Y. (3) $\times 10^2$	T.75 (4)	INTENSITY (in watt ml^{-1}) Vs. Time (Min.) 0	2	4	10	20	30
.005	.05	106	1.45	25	656	116	101	93	101	124
		114	1.55	25	656	132	101	108	108	132
	.10	280	1.90	12	1583	250	286	294	116	124
		280	1.91	12	1814	240	270	278	124	116
	.15	541	2.46	12	2308	294	340	448	39	54
		539	2.45	13	1999	301	325	456	47	62
	.20	713	2.43	24	2385	317	311	278	363	108
		786	2.68	28	1845	301	301	332	263	54
.006	.05	104	1.42	24	588	115	86	93	79	115
		88	1.20	24	566	101	108	79	93	86
	.10	241	1.65	12	1683	201	208	251	115	115
		252	1.72	12	1748	208	244	258	115	101
	.15	389	1.77	14	2213	244	273	330	50	58
		359	1.64	15	1784	229	258	323	50	50
	.20	649	2.22	24	3431	244	237	222	287	115
		584	1.99	25	1784	244	222	201	301	136

(1) Concentrations of 16,17-didecyloxyviolanthrone (DDV) and bis(2,4,5-trichloro-6-carbopentoxyphenyl oxalate (CPPO) are in the chemiluminescent reaction containing .375 M H_2O_2 and 7.5 x 10^{-4} M sodium salicylate as catalyst. Solvent system was 75% dibutyl phthalate, 20% dimethylphthalate, 5% t-butyl alcohol.

(2) Radiation capacity in joules $liter^{-1}$.

(3) Chemiluminescent quantum yield in einsteins $mole^{-1}$.

(4) Time for 75% of the total radiation to be emitted.

Figure 1: Effect of DDV Concentration on Spectral Distribution of IR Chemiluminescent Reaction[1]

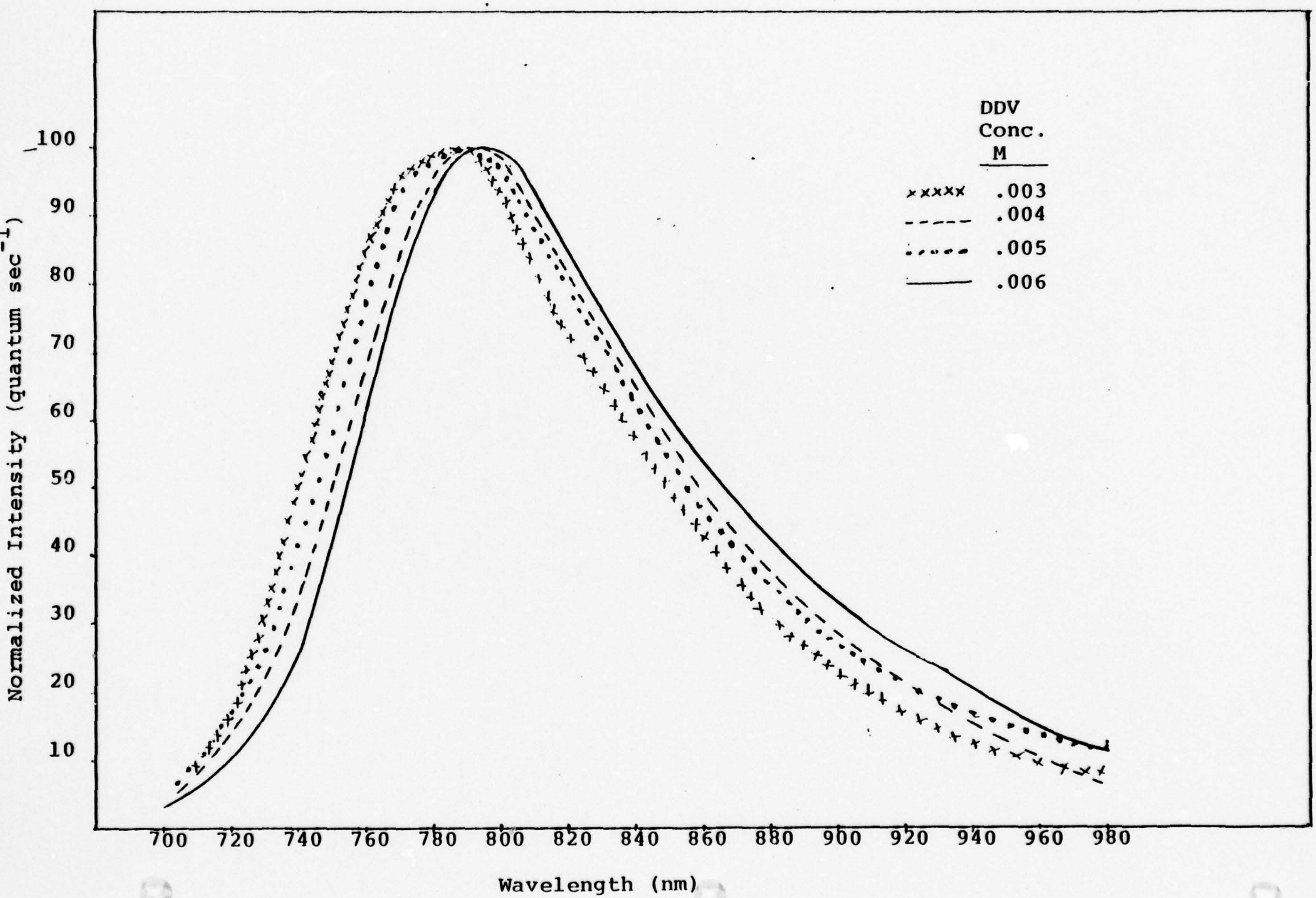


Figure 1: Effect of DDV Concentration on Spectral Distribution of IR Chemiluminescent Reaction[1]

[1] Chemiluminescent reactions contained .15 M bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate(CPPO), the indicated concentrations of 16,17-didecyloxyviolanthrone (DDV), .375M H_2O_2 and 7.5 x 10^{-4}M sodium salicylate catalyst.

Solvent system was 75% dibutyl phthalate, 20% dimethyl phthalate, 5% t-butyl alcohol. Spectra are corrected for intensity decay.

TABLE 4

CHEMILUMINESCENCE PERFORMANCE OF NEW OXALIC ACID DERIVATIVES[1]

COMPOUND	CONC. M	RC[2]	Q.Y.[3] x 10^2	T.75[4]	INTENSITY (microwatts ml^{-1}) Vs Time (Min.) 0	.5	1	2	3	4	10	20	30
bis(2,4-dinitro-6-carbopentoxyphenyl)oxalate (7)	.075	27.2	0.20	17	58.9	38.3	42.2	36.3	31.0	26.1	14.6	10.2	8.4
6-butoxy carbonyl-5,7,8-trichloro-1,4-benzodioxan-2,3-dione (5)	.075	.32	0.003	.06	85.8	.42	.14						
2',2",3',3",4',4",5',5",6',6"-deca fluoro-N,N'-bis(trifluoromethylsulfonyl) oxamide (9)	.075	2.24	.02	1	28.4	26.8	11.8	3.66	1.12	.47			

1 Chemiluminescent reactions contained .006M 16,17-didecyloxyviolanthrone (DDV), the indicated concentrations of the oxalic acid derivatives, .375M H_2O_2 and 5 x 10^{-4}M sodium salicylate catalyst. Solvent contained 75% dibutyl phthalate, 20% dimethyl phthalate and 5% t-butyl alcohol.

2 Radiation capacity in joules $liter^{-1}$.

3 Chemiluminescent quantum yield in einsteins $mole^{-1}$.

4 Time required for 75% of the total radiation to be emitted.

Experimental

Spectra and quantum yields for both chemiluminescence and fluorescence were obtained according to procedures previously described using a modification of the spectro-radiometer originally described by Roberts and Hirt.[15] The instrument employed a Jarrell-Ash Model 82-410 monochromator and an RCA C313034 photomultiplier with a gallium arsenide photocathode operated with dry ice cooling. The monochromator and photomultiplier were corrected for wavelength response by calibration against an Optronics Laboratories Model 245C 45 watt tungsten-halogen lamp traceable to an NBS standard of spectral irradiance. The reported quantum yield of quinine sulfate was used as the fluorescence standard. Chemiluminescence and fluorescence are thus corrected for wavelength response of the instrument.

Infrared spectra were recorded on a Perkin-Elmer Model 297 spectrophotometer. Nmr spectra were obtained on a Varian EM-360A instrument. Melting points were determined on a "Mel-Temp" block and are uncorrected.

16,17-Didecyloxyviolanthrone (DDV)

16,17-Dihydroxyviolanthrone (12.5 g, .026 mol), 25.0 g (.360) of anhydrous potassium carbonate and 100 ml DMF were placed in a 500 ml 3-neck round bottom flask fitted with a reflux condenser, thermometer, nitrogen inlet and mechanical stirrer. The mixture was heated to 100° under nitrogen and a solution of 21.0 g (.095 mole) of 1-bromo-n-decane in DMF was added while heating to 130°. After the addition was complete, the mixture was held at 135-140° for 16 hr.

16,17-Didodecyloxyviolanthrone

16,17-Dihydroxyviolanthrone (12.5 g, .026 mol; source: BASF), 25.0 g (.36 mol) anhydrous potassium carbonate and 100 ml of DMF were charged into a 500 ml flask fitted with mechanical stirrer, addition funnel, thermometer and nitrogen inlet. The mixture was heated under a nitrogen atmosphere to 100^{o} at which point 25.0 g (0.100 ml) of 1-bromo-n-decane was added over 45 min. The mixture was stirred at 135-140^{o} for 17 hours under nitrogen. The hot reaction mixture was poured into a 2 liter beaker and 1.8 l of distilled water was added, precipitating a dark blue solid which was filtered, washed and re-digested with about 1 l of warm distilled water and filtered. The solid on the filter was washed with methanol and dried yielding 17.7g of crude product, mp 142-150. The crude product was extracted for 5 hours in a Soxhlet apparatus with dichloromethane. Evaporation of the solvent yielded a dark blue solid which after washing methanol and petroleum ether afforded 16.2g of solid, mp 138-145. Eight g. of this solid was recrystallized from 650 ml of butyl acetate affording 3.90g of product, mp 144-7^{o}. Recrystallization from ethanol afforded analytically pure 16,17-didodecyloxyviolanthrone mp 150-153. Calcd for $C_{58}H_{64}O_4$: C, 84.43; H, 7.82.

Found: C, 84.32; H, 8.03.

The cooled reaction mixture was then transferred to a 2 l beaker digested with about 1.8 l of distilled water, filtered, washed with methanol and re-digested with warm water and filtered, washing with methanol. Crude yield was 18.95 g. The crude product was extracted in a Soxhlet with 400 ml of dichloromethane yielding 13.15 g of material. Successive recrystallization from butyl acetate, butyl alcohol and methyl cyclohexane gave analytically pure 16,17-didecyloxyviolanthrone (DDV) mp 158-61°.

Anal Calcd. for $C_{54}H_{56}O_4$: C, 84.37; H, 7.34.

Found: C, 84.22; H, 7.31.

Several samples of DDV although pure by elemental analysis and thin layer chromatography, still showed a small amount of visible light in the chemiluminescent reaction. Purification was accomplished on a Waters 500 Preparative Liquid Chromatograph loading 8g of once recrystallized (dimethylacetamide) DDV onto 2-500 cc silica gel columns in series eluting first with dichloromethane (15 l) and finally with 1% methanol in dichloromethane. Three cycles and a final recrystallization (n-butanol) were required for complete removal of the visible fluorescent impurities. Recovery was 2.9 g (36%).

16-Hydroxy-17-decyloxyviolanthrone

A suspension of 8.6 g (.018 mol) of 16,17-dihydroxyviolanthrone in 50 ml DMF was stirred for 30 min at 60-65° and while stirring 4.0g (.019 mol) of silver perchlorate in 10 ml DMF was added dropwise over 30 min. Stirring was continued for 2 hr at 65°, the mixture cooled, filtered and the mono silver salt washed with ethanol. Yield was 8.9g (85%).

Anal Calcd for $C_{34}H_{15}O_{4}Ag$: Ag, 18.1.

Found: Ag, 15.9, 16.1.

A mixture of 10.0 g (.017 mol) of the silver salt prepared above and 10 ml (12.6g, .047 mol) of n-decyl iodide in 75 ml of 1-nitropropane was stirred overnight at reflux. The reaction mixture was cooled to room temperature and a solid filtered, washed with methanol and digested in aqueous sodium thiosulfate (which can be preceded by a sodium cyanide digestion) to give 9.1 g(86%) of crude product. Three g of this material was recrystallized from 50 ml of trichlorobenzene affording 0.6 g of a dark purple solid, mp 208-11 (overall yield was 17%). The analytical sample was recrystallized from toluene (nitroethane may also be used) without change in mp.

Anal Calcd. for $C_{44}H_{36}O_{4}$: C, 84.05; H, 5.77.

Found: C, 83.43; H, 5.78.

16-Hydroxy-17-Dodecyloxyviolanthrone

The procedure described above for the decyl monoether was used for the preparation of 16-hydroxy-17-dodecyloxyviolanthrone, mp 201-4 (toluene).

Anal Calcd. for $C_{46}H_{40}O_4$: C, 84.12; 6.14.

Found: C, 83.73; H, 6.00.

16,17-Di(4-carboxyethoxybutyl)violanthrone (CBV)

A 500 ml round-bottom flask fitted with stirrer, condenser, thermometer and N_2 purge inlet was charged with 15.0 g (.031 ml) of 16,17-dihydroxyviolanthrone, 30g anhydrous potassium carbonate and 150 ml DMF (dried over molecular sieves and $MgSO_4$). The contents were heated to 100°C with stirring followed by dropwise addition of a solution of 25g (.12 ml)ethyl-5-bromo-valerate in 45 ml DMF. The mixture was heated to 135°C. and stirred for 2 hours. The DMF was decanted from the flask and the flask residue was washed with chloroform. Evaporation of the solvents left a residue which was dissolved in 800 ml chloroform and extracted with water until the chloroform layer had little or no apparent turbidity. The chloroform was distilled out and the residue taken up in 500 ml benzene. The solution was filtered hot through a bed of "Hy-Flo"[R] filtering aid and the cake rinsed with 50 ml benzene. The filtrate was treated with 1 g of Darco G-60 and 1 g of Super-Filtral[R], then heated to a boil and filtered through Hy-Flo. The solid on the filter was then washed with 150 ml hot benzene and the filtrate was concentrated to 425 ml and 150 ml heptane added. The solution volume further concentrated to 350 ml by evaporation.

On standing overnight, the solution deposited crystals which were isolated by filtration and washed with 100 ml heptane. This filtrate was charged with an additional 50 ml heptane and the total solution volume then reduced to 250 ml and cooled, resulting in the deposition of black crystals, which were filtered giving 5.6 grams (25%) of 16,17-Di(carboxy-ethoxybutyl)violanthrone (CBV). Recrystallization from a benzene/violanthrone (CBV). Recrystallization from a benzene/heptane mixture afforded the pure sample, m.p. = 164°C., pure by thin layer chromatography.

Anal Calcd. for $C_{48}H_{40}O_8$: C, 77.40; H, 5.41.

Found: C, 77.53; H, 5.44.

6-Nitro-1,4-benzodioxan-2,3-dione

A mixture of 4-nitro catechol (20g, 0.13 mol and triethylamine (13.1 g, 0.13 mol) in 50 ml tetra-hydrofuran was cooled to 0-5°C. A solution of 16.5g (0.13 mol) oxalyl chloride in 25 ml tetrahydrofuran was added over 30 minutes. The mixture was allowed to come to room temperature and stirred overnight. The mixture was filtered and the solvent evaporated from the filtrate under reduced pressure. The product was recrystallized twice from ethylene dichloride, mp 150-152°dec. The product is extremely moisture sensitive and must be stored in a dessicator.

Anal Calcd. for: $C_8H_3NO_6$: C, 45.95; H, 1.44; N, 6.70.

Found: C, 42.82; H, 2.45, N, 5.85.

6-chloro-1,4-benzodioxan-2,3-dione

4-Chloro catechol, 20 g(0.14 mole), triethylamine 14.1g. (0.14 mole) in 100 ml of tetrahydrofuran were stirred and cooled in an ice bath. A solution of oxalyl chloride 17.6g (0.14 mole) in 50 ml tetrahydrofuran was added over thirty minutes. The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered and solvent was removed from the filtrate under reduced pressure. The resulting solid was recrystallized twice from methyl cyclohexane, yielding the desired ester mp 122-126^{o}.

Anal Calcd. for: $C_8H_3O_4Cl$: C, 48.39; H, 1.52; Cl, 17.86.
Found: C, 50.43; H 2.22; Cl, 15.82.

IR (nujol): carbonyl doublet at 1790 cm^{-1}.

5-Pentoxycarbonyl-1,4-benzodioxan-2,3-dione

3-Pentoxycarbonyl (22.4 g, .1 mol) catechol, 75 cc. of tetrahydrofuran and 10g. (0.1 mol) of triethylamine were stirred and cooled to 0-5^{o}. A solution of 12.8g (0.1 mole) of oxalyl chloride in 25 ml of tetrahydrofuran was added over 30 minutes at 0-5^{o}. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered, then the solvent was evaporated from the filtrate under reduced pressure. The solid residue was recrystallized from cyclohexane twice yielding 11.5g (51%) of the ester mp 90-92^{o}.

Anal Calcd for $C_{14}H_{14}O_6$: C, 60.4; H, 5.07.
Found: C, 59.6; H, 5.47.

IR (nujol): carbonylr at 1760 cm^{-1} and 1700 cm^{-1}.

3-Pentoxycarbonyl catechol

A mixture of 50g (0.32 mol) of 2,3-dihydroxybenzoic acid, 31.7g (0.39 mol) n-pentanol, 200 ml toluene and 5 ml sulfuric acid was refluxed for 36 hr. After cooling the mixture was dissolved in ether and washed with water. After separation of the ether and evaporation under reduced pressure, the oil was distilled (117-118^{o} at 0.5 mm)affording 40.3 of a colorless oil. IR indicated hydroxyl at 3450cm^{-1} and carbonyl at 3450 cm^{-1}.

Anal Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19.

Found: C, 62.26; H, 6.92.

4-Butoxycarbonyl catechol

A mixture of 3,4-dihydroxy benzoic acid (154 g, 1.0 mol) n-butanol (88.8g, 1.2 mol), toluene (500 ml) and conc. sulfuric acid (10 mol) was refluxed using a Dean-Stark trap for 18 hours, collecting 30 ml of H_2O. The reaction mixture was cooled and the crystals that formed isolated by filtration, washed with water, 5% sodium carbonate and again with water. Recrystallization twice from toluene afforded 139.4g (66%) of light tan crystals, mp 116-118^{o}.

IR(nujol) of starting acid: carbonyl bands at 1830 cm^{-1} and 1700 cm^{-1}.

IR(nujol) of product: carbonyl bands at 1680 cm^{-1} and 1600 cm^{-1}.

4-Butoxycarbonyl-3,5,6-trichloro catechol

4-Butoxycarbonyl catechol (21g, 0.1 mol) and sulfuryl chloride (45.6 g, 0.33 mol) were stirred and heated in an oil bath at 85^{o} for two hours. After cooling, the excess sulfuryl chloride was removed under reduced pressure yielding an oily residue. The oil crystallized on standing and was recrystallized from heptane, cyclohexane, and hexane once again, mp 90-91^{o}. NMR shows absence of aromatic protons.

Anal Calcd. for: $C_{11}H_{11}Cl_3O_4$: C, 42.13; H, 3.54; Cl, 33.92.
Found: C, 42.16; H, 3.55; Cl, 32.99.

6-Butoxycarbonyl-5,7,8-trichloro-1,4-benzdioxan-2,3-dione

4-Butoxycarbonyl-3,5,6-trichloro catechol (12 g, 0.038 mol), triethylamine (3.9g., 0.038 mol) in 60 ml tetrahydrofuran were stirred and cooled to 0-5^{o}. A solution of oxalyl chloride (4.8 g., 0.038 mol) in 20 ml tetrahydrofuran was added over 40 minutes. The reaction mixture was allowed to warm to room temperature, stirred overnight and filtered. Solvent was removed from the filtrate under reduced pressure yeilding an oil resulted which crystallized on standing. Recrystallization twice from cyclohexane containing a small amount of toluene afforded 13 g.(93%) of the oxalate ester, mp 142-144^{o}.

Anal Calcd. for $C_{13}H_9Cl_3O_6$: C, 42.48; H, 2.45; Cl, 28.95.
Found: C, 42.20; H, 2.97; Cl, 27.66.

IR(nujol): carbonyl doublet at 1810 cm^{-1} and a carbonyl at 1720 cm^{-1}.

4-Pentoxycarbonylcatechol

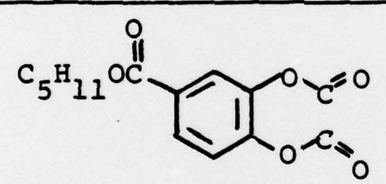
A mixture of 24.3g (0.16 mol of 3,4-dihydroxy benzoic acid, 15.5g of n-pentanol (0.176 mole), 100 cc. of toluene and 2 cc. of conc. sulfuric acid was refluxed over an azeotrope head for three hours. A total of 4.5 cc of water was collected. (Theoretical amount of water is 2.9 cc). The mixture was cooled to 0-5^{o}C, filtered and washed with hexane. Recrystallization from toluene afforded 14.8g (41%) of pure material mp 98-99.5^{o}.

Anal Calcd for $C_{12}H_{16}O_4$: C, 64.27; H 7.19.

Found: C, 64.25; H 7.07

IR (nujol): carbonyl 1660 cm^{-1}

6-Pentoxycarbonyl-1,4-benzodioxan-2,3-dione



A mixture of 11.2g (0.05 mol) of 4-carbopentoxycatechol, 5 g. (0.05 mol) of triethylamine and 75 cc of dry dioxane was stirred at room temperature. A solution of 6.4g (0.05 mol) oxalyl chloride in 50 cc of dry dioxane was added to the above over 40 minutes. When addition was complete, the reaction mixture was heated to reflux, and allowed to cool to room temperature. The triethylamine hydrochloride was filtered, yielding 6.2g was collected (theory 6.8g). Evaporation of the solvent from the filtrate under vacuum yielded an oil which was crystallized from cyclohexane afforded 5g of pale yellow crystals mp 108-110^{o}C.

Anal Calcd. for $C_{14}H_{14}O_6$: C, 60.4; H 5.07.

Found: C, 59.98; H 5.38.

IR(nujol): carbonyl, doublet at 1790 cm^{-1}.

Pentyl-3,5-dinitrosalicylate

Into a 50 ml Erlenmeyer flask was charged 10.4g of HNO_3(90%) and 30g H_2SO_4 (96%), stirred and cooled to -10°C. n-Pentyl salicylate was added dropwise until the temperature reached 5°C, at which point the mixture was cooled again to -10°C and additional pentylsalicylate added. After 5g of pentylsalicylate was added, the mixture turned yellow and became viscous. After a total of 11.5g (55.1 mole) pentylsalicylate had been added, the mixture deposited a yellow precipitate. The mixture was quenched on 100g ice and the yellow solid filtered and washed with water until the washes were neutral. This gave 13.3g (81%) of crude 3,5-dinitropentylsalicylate, m.p. = 34-36°C. Recrystallization from methylcyclohexane afforded the pure material, mp 34-35.5°.

Anal Calcd. for $C_{12}H_{14}N_2O_7$: C, 48.33; H, 4.73; N, 9.33

Found: C, 48.78; H, 4.73; N, 9.32

nmr ($CDCl_3$): 0.4-2.2, broad m, 9H; 4.5, t, 2H; 9.05, s, 2H; 12.78, S, 1H.

Bis(3,5-dinitro-6-carbopentoxyphenyl)oxalate

A 100-ml. round-bottomed 3-neck flask, fitted with thermometer, addition funnel and nitrogen inlet was purged with N_2, and charged with 25 ml toluene and 7.65g (25.7 mmole) of pentyl-3,5-dinitrosalicylate. When solution was complete, the flask was charged with 2.6g (25.7 mmole) of triethylamine over a period of 20 minutes. The temperature gradually rose to 32°C. and the mixture was stirred 15 minutes. A solution of 2.18g (17.2 mmole, 34% excess) of oxalyl chloride in 15 ml toluene was then added dropwise over 20 minutes.

The mixture was stirred 18 hours, filtered, and the precipitate washed with 100 ml toluene. Evaporation of the solvent under reduced pressure left an orange oil. Hexane (50 ml) was added with stirring until a tan solid precipitated. The solid was filtered and rinsed with several small portions of hexane affording 6.0g (72%) of bis(3,5-dinitro-6-carbopentoxyphenyl)oxalate, mp 135-140^{o}. Recrystallization from methylcyclohexane gave the pure material mp 144-145^{o}.

Anal Calcd. for $C_{26}H_{26}N_4O_{16}$: C, 48.01; H, 4.03; N, 8.61.

Found: C, 47.91; H, 4.06; N, 8.40

ir(Nujol): 1775, 1718, 1538, 1340 cm^{-1}.

nmr($CDCl_3$); 0.7-2.3, m, 9H; 4.5, t, 2H (J=2.5Hz); 9.2, s, 2H.

α,α,α,2,3,4,5,6-octafluoro methanesulfonanilide

Pentafluoro aniline 20g. (0.11 mol) was dissolved in 25 ml of dichloromethane and cooled to 0-5^{o}. Trifluoromethane-sulfonic anhydride 30.9g (0.11 mol) in 25 cc of dichloromethane was added keeping the temperature at 0-5^{o}. When the addition was complete, triethylamine 11.1g (0.11 mole) in 25 cc of dichloro-methane was added at 0-5^{o}C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum and the resulting oil was extracted three times with diethyl ether. Evaporation of the ether under reduced pressure left an oily product which was distilled under reduced pressure. The middle fraction (bp 76-80^{o} at 0.6 mm)weighed 15.7g and solidified to a crystalline solid, mp 68-69.5^{o}.

Anal Calcd. for $C_7HNSO_2F_8$: C, 26.68; N, 4.44; S, 10.12, F, 48.23.

Found: C, 26.27; N, 4.55; S, 9.89; F, 45.17.

2',2",3',3",4',4",5',5",6',6"-decafluoro-N,N'-bis [(trifluoromethyl)sulfonyl] oxanilide

2,3,4,5,6-Octafluoro-methanesulfanilide was dissolved in 30 cc of tetrahydrofuran and 1.5g (0.015 mol) of triethylamine was added. The mixture was cooled to 0-5^{o} and 0.95g (0.015 mole) of oxalyl chloride in 20 cc of tetrahydrofuran was added over thirty minutes. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solid was filtered, washed with tetrahydrofuran then the cake was discarded. Evaporation of the solvent from the filtrate solid which was recrystallized from cyclohexane mp 107-110^{o}.

Anal Calcd. for $C_{16}F_{16}N_2S_2O_6$: C, 28.08; F, 44.42; N, 4.09, S, 9.37.
Found: C, 28.59; F, 41.99; N, 4.84; S, 9.06.

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